



Separation of trivalent actinides and lanthanides using dithiophosphinic acids - End of Studies Project

Philippe Marc

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Separation of trivalent actinides and lanthanides using dithiophosphinic acids

End of Studies Project

Philippe Marc
2010-2011



Abstract

This report presents the results of the degradation study of the active compound of the commercial extractant CYANEX® 301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid.

It was determined that the complete degradation, which is commonly thought to produce the oxo equivalent, is in fact a two-step process where the first product to be obtained is relatively stable and corresponds to a condensation more than a degradation.

A study on the impact of some parameters of the condensation, such as the concentration of oxidizer or acid and the atmosphere, has enabled us to propose here a general equation of the degradation of CYANEX® 301.

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Acknowledgments

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All my thanks also go to the people who have worked for enabling this internship to take place: Dr. Dominique Warin and Pr. Christophe Poinssot at the French Alternative Energies and Atomic Energy Commission, Dr. Emory Collins at Oak Ridge National Laboratory, Toynette Bird and Brenda Goodman at the Oak Ridge Institute for Science and Education, and all the other persons I forgot.

And to finish, I would like to thank all the members and coworkers of the Chemical Separation Group for their warm welcome, and their patience during my trials and errors in English!



Figure 1 - Chemical Separation Group

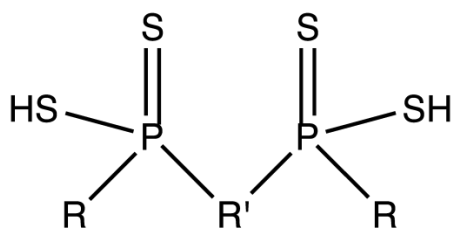
Introduction

Organophosphorus compounds are very commonly used in hydrometallurgy. The properties of these molecules make them primary choices for extracting metallic cations, their selectivity in some cases also allowing them to be part of some separation processes involving these elements. We can give the example of TBP (*TriButyl Phosphate*) which, used in the PUREX process, extracts selectively uranium and plutonium from the aqueous stream that comes from the dissolution of spent nuclear fuels in nitric acid.

These properties and the applications that resulted make these compounds potential candidates for advance recycling of spent nuclear fuels [1]. Indeed, with the deployment of 4th generation nuclear reactors, it is planned to keep recycling uranium and plutonium contained in the spent fuel, and to start recovering minor actinides (neptunium, americium and potentially curium). The key step of such a process will be the separation of the actinides of interest from the lanthanides.

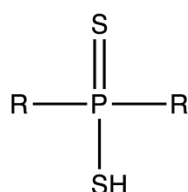
In this context, researches, led to improve the extraction capacities and the selectivity of the molecules, have shown that rigidifying the ligand (by use of molecular engineering) in the position it adopts when the complex is formed can significantly improve its extraction ratio and selectivity [2] [3]. We can also point out that if the complex is made of several ligands, synthesizing a molecule with the same number of chelating groups and rigidifying it in the optimal position enable an important improvement of distribution performance. These results have sparked studies on the improvement of the extraction ratios, by pre-positioning, of other chelates.

Optimized bisdithiophosphinic acids (Figure 2) were synthesized for extraction, but seemed to exhibit poor extraction and selectivity behavior. The question of a possible degradation lowering these capacities of the molecules has been hypothesized. Considering this possibility, it has been decided to go back to the commercially available monodithiophosphinic acids and proceed with the study of degradation.



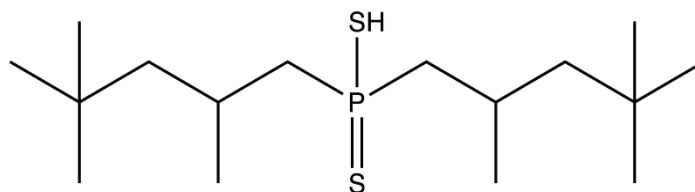
[Figure 2 - Bisdithiophosphinic Acid](#)

Researches [4] have been conducted on molecules of dithiophosphinic acid (Figure 3). But when extraction experiments were run in nitric acid media, it has been observed that the product appears to degrade very rapidly, making these molecules impossible to use in such processes. A search in the literature has shown that no study has been led on the degradation mechanism and products of dithiophosphinic acid molecules. Judging from this lack of knowledge, it has been decided to study this degradation. The results of such studies are expected to lead to solutions to improve the resistance of these molecules.



[Figure 3 - Dithiophosphinic Acid](#)

In order to answer this question, we have used bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Figure 4), which is the main compound of CYANEX® 301 extractant. For the rest of this report, we will use the term “CYANEX® 301” to refer to bis(2,4,4-trimethylpentyl)dithiophosphinic acid, obtained by purifying the commercial CYANEX® 301.



[Figure 4 - CYANEX 301 \(Bis\(2,4,4-trimethylpentyl\)dithiophosphinic Acid\)](#)

Chapter 1: Oak Ridge National Laboratory

I. The laboratory

Oak Ridge National Laboratory, abbreviated ORNL, is one of the Department of Energy national laboratories (Figure 5). These facilities are overseen by the United States Department of Energy, for the purpose of advancing science and helping promote the economic and defensive national interests of the United States of America. ORNL is managed by UT-Battelle



Figure 5 – Oak Ridge National Laboratory

This system of centralized national laboratories has been initially created in order to coordinate scientists' efforts for solving wartime scientific problems, such as the development of RADAR or atomic weapons. ORNL was established in 1943 within the framework of the Manhattan Project, with the mission of separating uranium isotopes for the first atomic bomb.

With the end of World War II and Cold War, these laboratories have turned their activities to new scientific problematic. Thus, ORNL now conducts research in the areas of:

- Neutron scattering
- High-performance computing
- Nanotechnologies
- Energy
- Biological systems
- Material sciences
- National security
- Chemical sciences
- Nuclear Physics

II. The Chemical Science Division

The Chemical Science Division is one of the 21 technical divisions of ORNL and conducts both fundamental and applied research using experimental, theoretical and computational approaches in all chemistry fields, such as:

- Chemical biosciences
- Fluid Interface Reactions, Structures and Transport
- Geochemistry and aqueous solution chemistry
- Heterogeneous catalysis
- Laser spectroscopy
- Mass spectrometry
- Materials chemistry
- Molecular transformations and fuel chemistry
- Neutron science, particular of soft materials
- Polymer, synthesis and characterization
- Radioactive materials characterization
- Separations chemistry
- Surface science and interfacial chemistry
- Theory, modeling and simulations



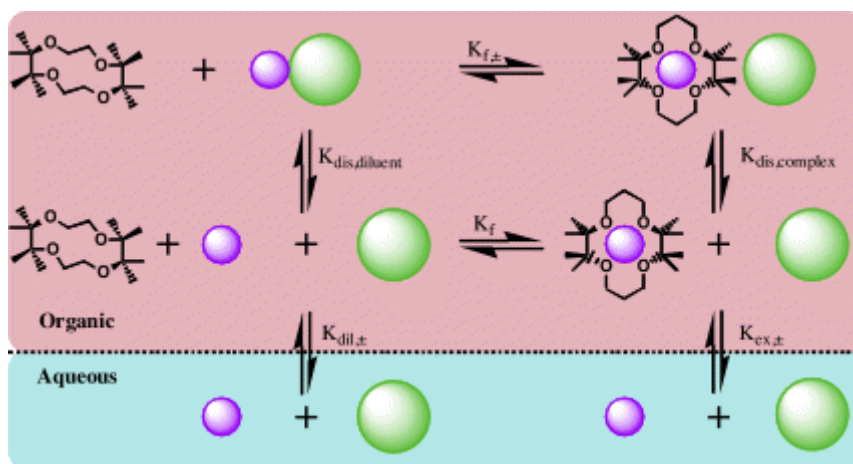
[Figure 6 - The new Chemical Science Division building](#)

III. The Chemical Separation Group

The Chemical Separation Group, within the Chemical Science Division, is specialized in extractions and separations using chemical processes and selective molecules. This includes cation separation (actinides/lanthanides for example).

To conduct these researches, the group creates new ligands, which involves organic synthesis, tests, and characterization using a wide variety of technics and instruments: X-ray diffraction to characterize the complex formed during extraction/separation, alpha, beta, and gamma radioanalytical methods...

The research studies of the group have, for example, led to the development of the famous CSSX process, which is now used at an industrial scale at the Savannah River site for the selective extraction of cesium from high-level waste.

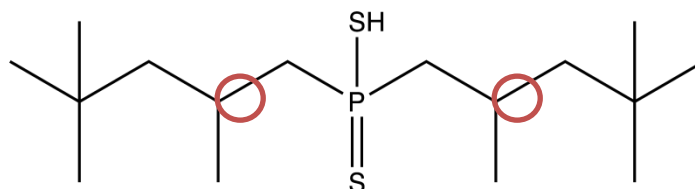


[Figure 7 - Chemical extraction and separation](#)

Chapter 2: Degradation of CYANEX® 301

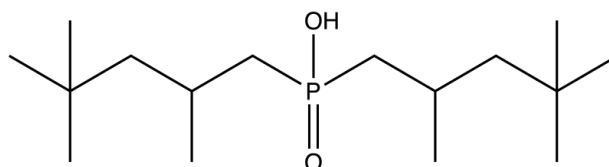
I. ^{31}P NMR characterization of commercial CYANEX® 272, 302, and of purified and ultra-purified CYANEX® 301

The commercial form of CYANEX® 301 is mainly composed of bis(2,4,4-trimethylpentyl)dithiophosphinic acid, with other impurities due to its synthesis or potential degradation. Commonly, the compound is purified using a protocol described in the appendix page 35, before any experiment is run. A sample of ultra-purified CYANEX® 301 was also received from INL (Idaho National Laboratory) where the major difference lies in the percentage of isomers found. While in purified samples of CYANEX® 301, all isomers [R;R],[S;S], [R;S] and [S;R] (asymmetric carbons are presented on Figure 8) are found, only the [R;R] and [S;S] isomers are present in a sample of ultra-purified CYANEX® 301. Ultra-purified CYANEX® 301 is crystalline and the corresponding crystal structure have shown the “layering of [R;R] and [S;S] sheets” [5].

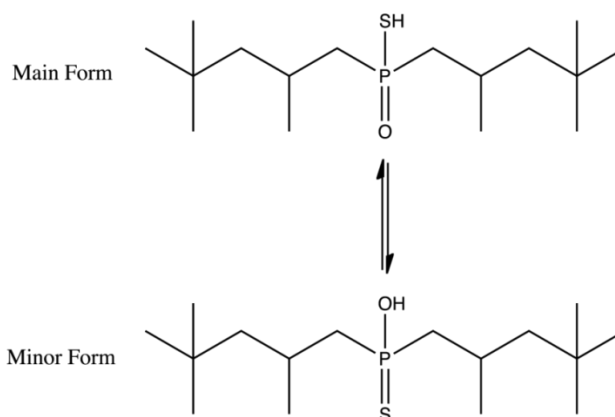


[Figure 8 - Asymmetric carbons of bis\(2,4,4-trimethylpentyl\)dithiophosphinic acid](#)

^1H decoupled ^{31}P NMR of these two products, alloy with those of CYANEX® 272 (bis(2,4,4-trimethylpentyl)phosphinic acid, Figure 9), and CYANEX® 302 (bis(2,4,4-trimethylpentyl)thiophosphinic acid, Figure 10), have been run. The spectra are presented in figures 11 to 14.



[Figure 9 - CYANEX® 272 \(Bis\(2,4,4-trimethylpentyl\)phosphinic Acid\)](#)



[Figure 10 - CYANEX® 302 \(Bis\(2,4,4-trimethylpentyl\)thiophosphinic Acid\)](#)

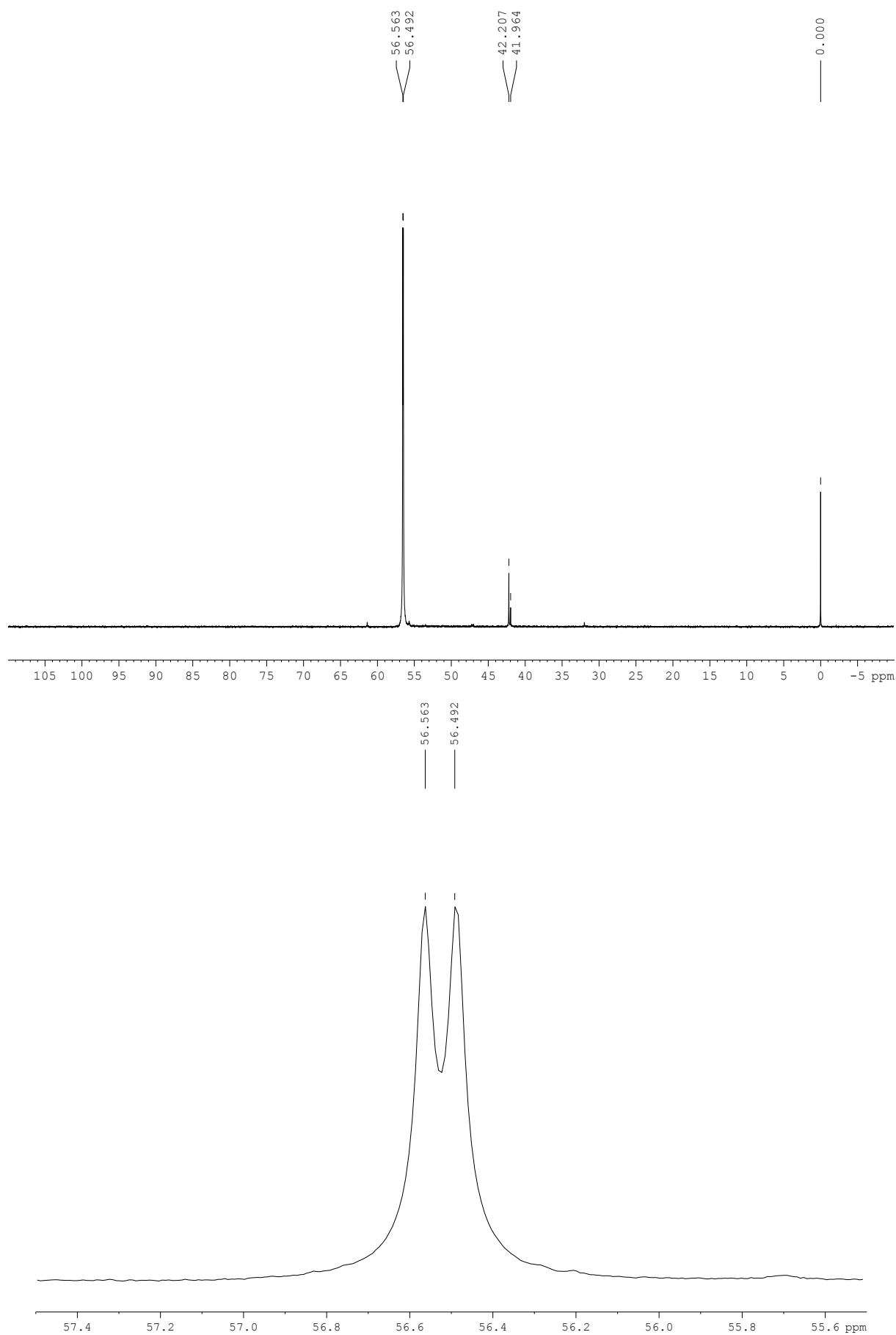


Figure 11 - CYANEX® 272 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O

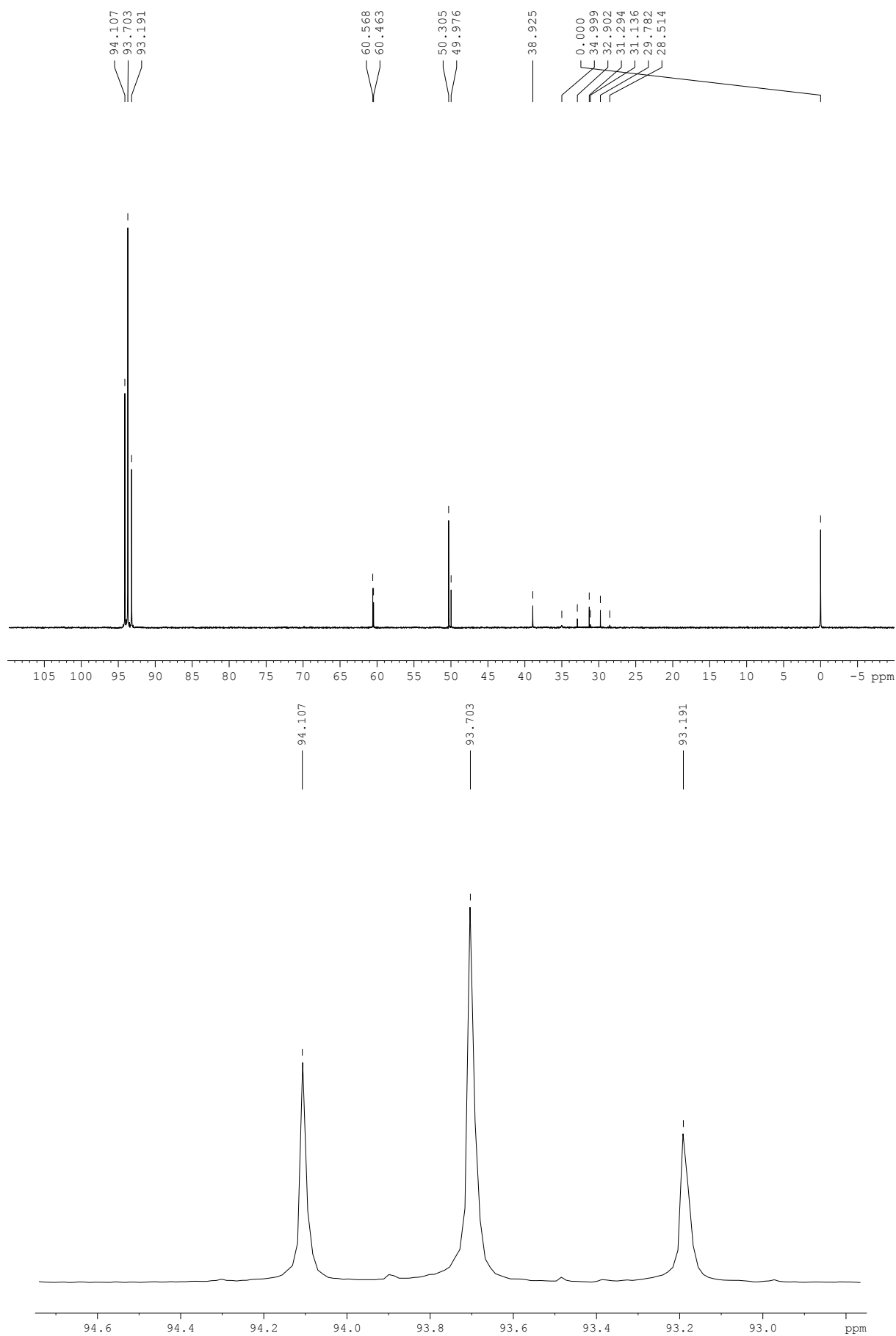
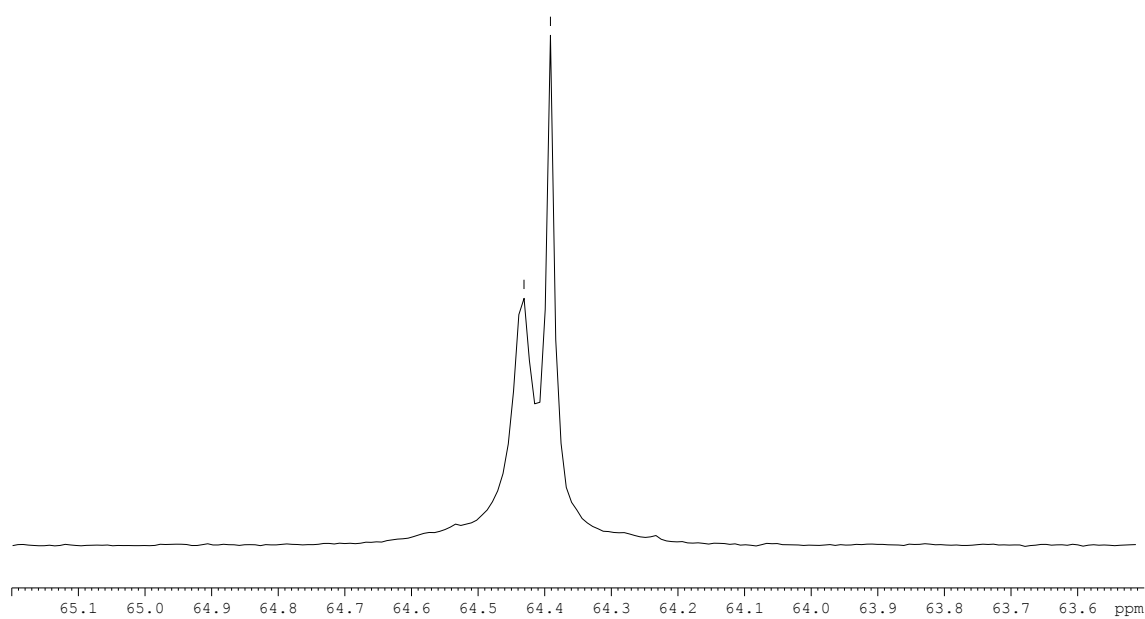
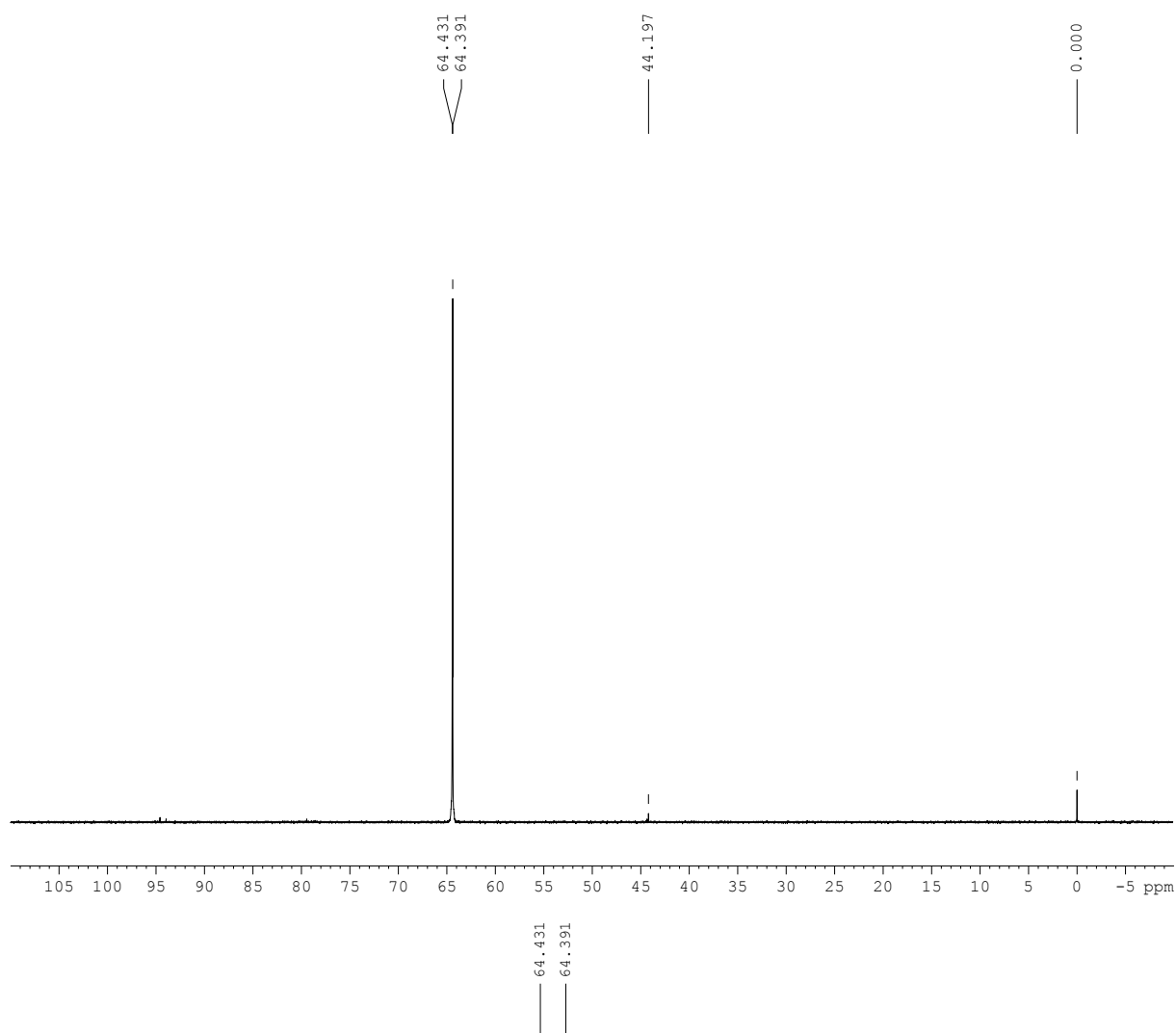


Figure 12 - CYANEX® 302 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O



[Figure 13 - Purified CYANEX® 301 0.1M in Toluene - ¹H Decoupled ³¹P NMR - Insert H₃PO₄ 0.1M in D₂O](#)

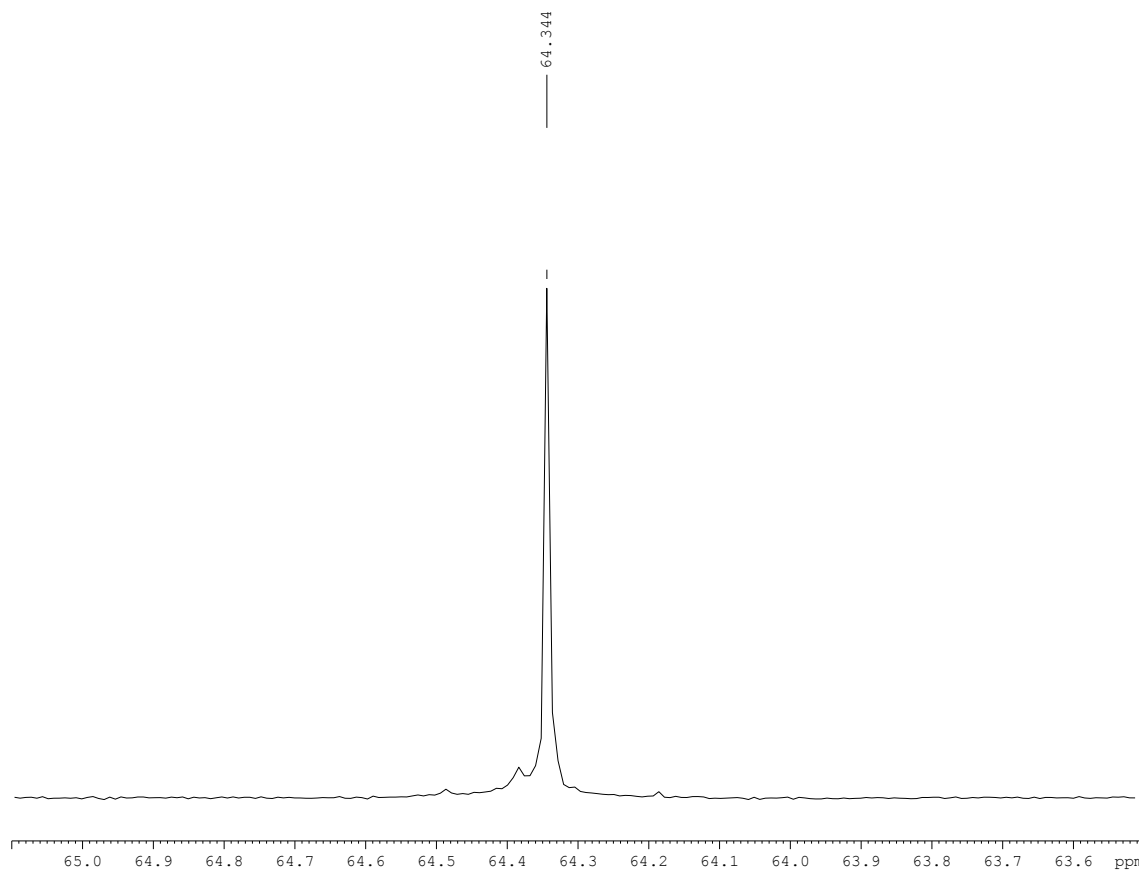
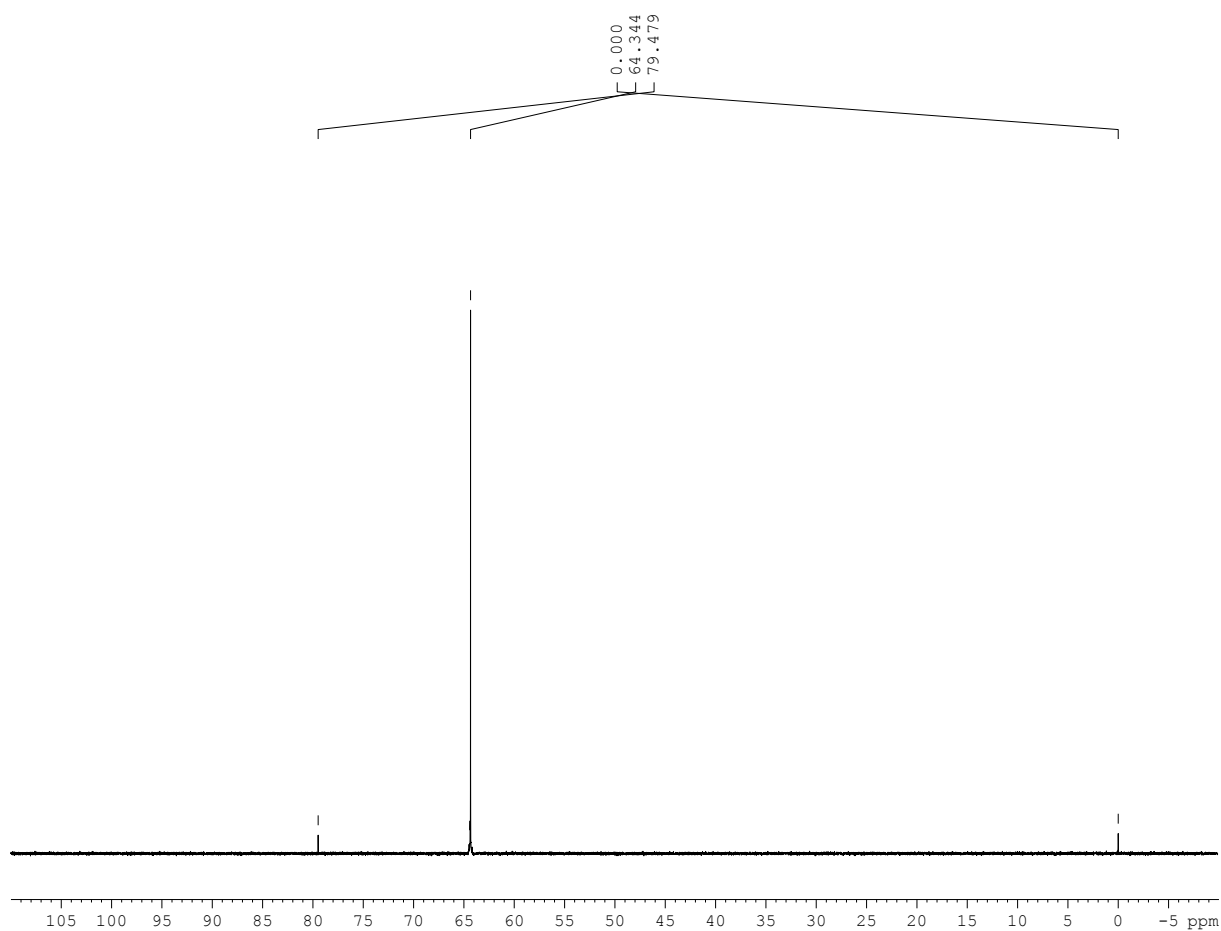


Figure 14 - Ultra-Purified CYANEX® 301 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O

It is interesting to point out the difference which appears between the purified and ultra-purified CYANEX® 301 on the spectra (Figures 13 and 14). Judging from the observations made with the XRD analysis on ultra-purified CYANEX® 301, we can assume that the second peak appearing in the spectrum of purified CYANEX® 301 is due to the other isomers present in the mixture, [R;S] and [S;R]. This can be explained by the fact the isomers [R;R] and [S;S] are mirror images, making of them a couple of enantiomers. Just as the previous isomers couple, the isomers [R;S] and [S;R] are also mirror images, and so, also a couple of enantiomers. These enantiomers are undistinguishable by NMR, therefore, these two couples being diastereoisomers of each other, they will give two different peaks for each couple. This is why only one peak appears on the spectra of the ultra-purified CYANEX® 301, and two on the purified spectra's.

This differentiation between the two couples also led to two peaks on the spectra of CYANEX® 272.

The spectra of CYANEX® 302 exhibit an important difference with those of CYANEX® 272 and 301. The reason of this difference lies on the fact that, the two chalcogen atoms are in this particular case different (one is sulfur, one is oxygen, instead of two sulfur or two oxygen atoms), this difference resulting in the addition of an asymmetric character to the phosphorous atom when the alkyl chains are [R;S] and [S;R]. This impact of the asymmetry of the phosphorous atom will be discussed in details in the explanation of the spectrum of the degradation product of CYANEX® 301.

This asymmetry can't be seen in the case of CYANEX® 301 and 272 because the proton born by the sulfur or the oxygen is involved in a fast exchange mechanism with the other sulfur or oxygen. This mechanism occurs too rapidly to distinguish the two discrete forms by NMR, which explains that only two peaks can be seen on the spectra of these products.

II. CYANEX® 301 degradation: analysis of the degradation product using ^{31}P NMR

1. NMR spectrums of the degraded products, and identification in the literature of the degradation product

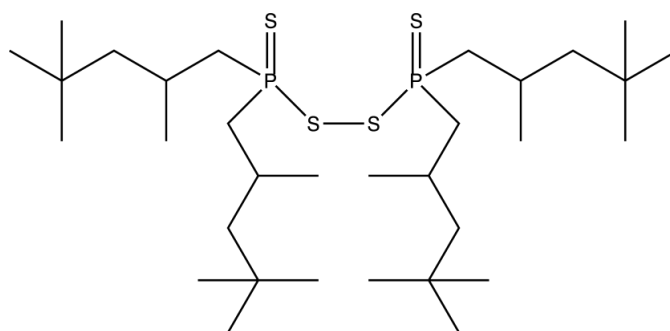
Several experiments of degradation of CYANEX® 301 have been run. In all these experiments, the same spectrum was always obtained after the degradation (Figure 16). The degradation experiments consisted in contacting solution of purified and ultra-purified CYANEX® 301 in toluene with nitric acid 2M during 3 hours, which ensured complete degradation.

Ultra-purified CYANEX® 301 was also tested for degradation (Figure 17). The spectrum of the product we obtained is presented page 16 (Figure 16).

A literature survey indicated that the degradation product would be CYANEX® 272, or CYANEX® 302 [6],[7]. But the comparison of the spectra of CYANEX® 272 and CYANEX® 302 with the spectrum obtained after the degradation clearly shows that we do not get either products.

A comparison of the ^{31}P NMR spectra corresponding to the degraded purified and ultra-purified CYANEX® 301 exhibited a clear difference (Figure 18). The purified CYANEX® 301 has a very complex multiplet (Figure 16), whereas the spectrum corresponding to the degraded ultra-purified CYANEX® 301 shows only one peak, with very low intensity peaks that appear very clearly in the spectrum of purified CYANEX® 301 (Figure 17). This observation has helped to propose the following explanation for the multiplicity of the peaks.

A more complete study of the literature has exhibited the possibility of a two-step degradation process [8] [9] [10] [11] [12], with the first leading to the formation of a disulfide bridge between two molecules of CYANEX® 301 (Figure 15).



[Figure 15 - Disulfide of Bis\(2,4,4-trimethylpentyl\)dithiophosphinic Acid](#)

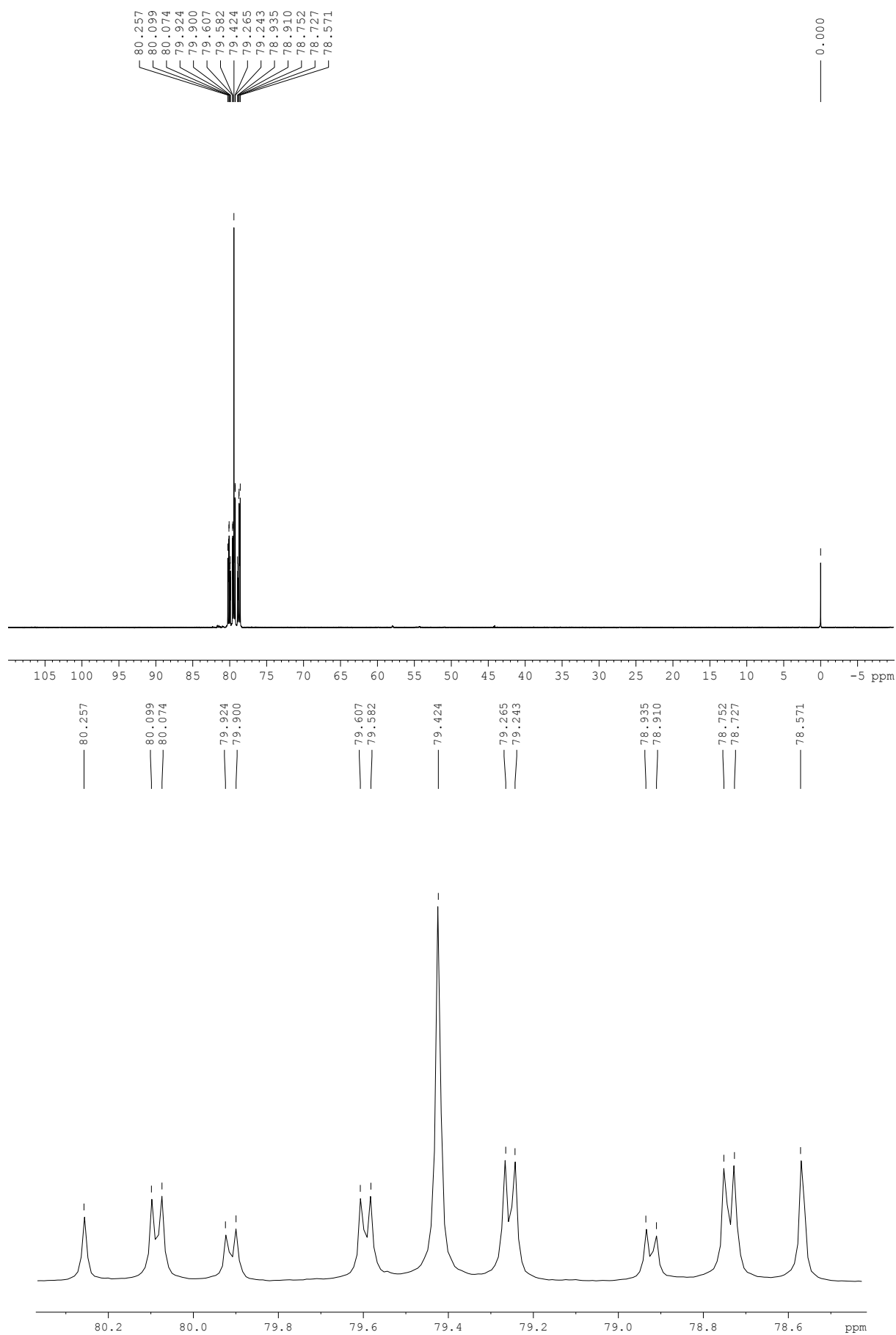


Figure 16 - Degraded Purified CYANEX® 301 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O

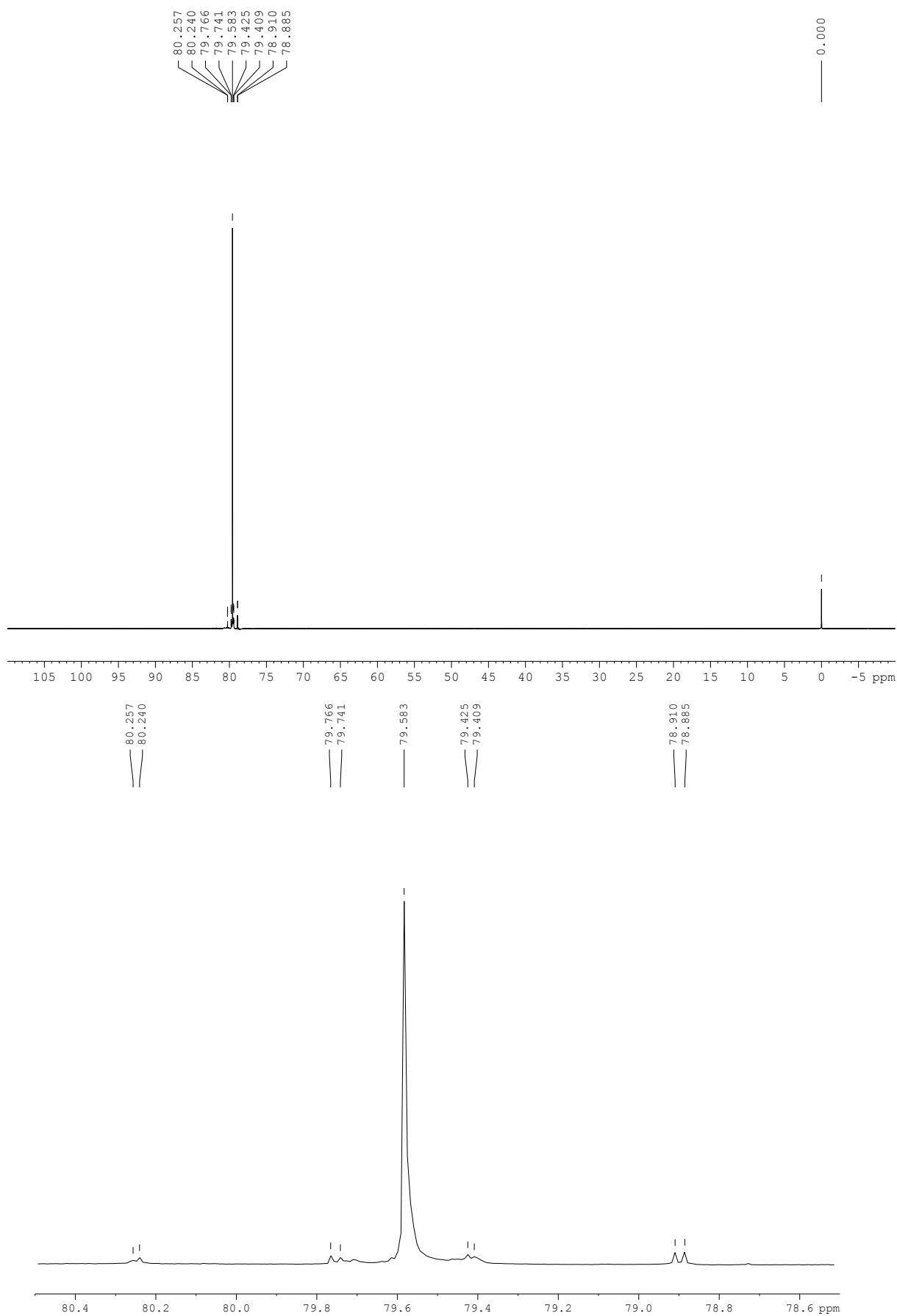


Figure 17 - Degraded Ultra-Purified CYANEX® 301 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O

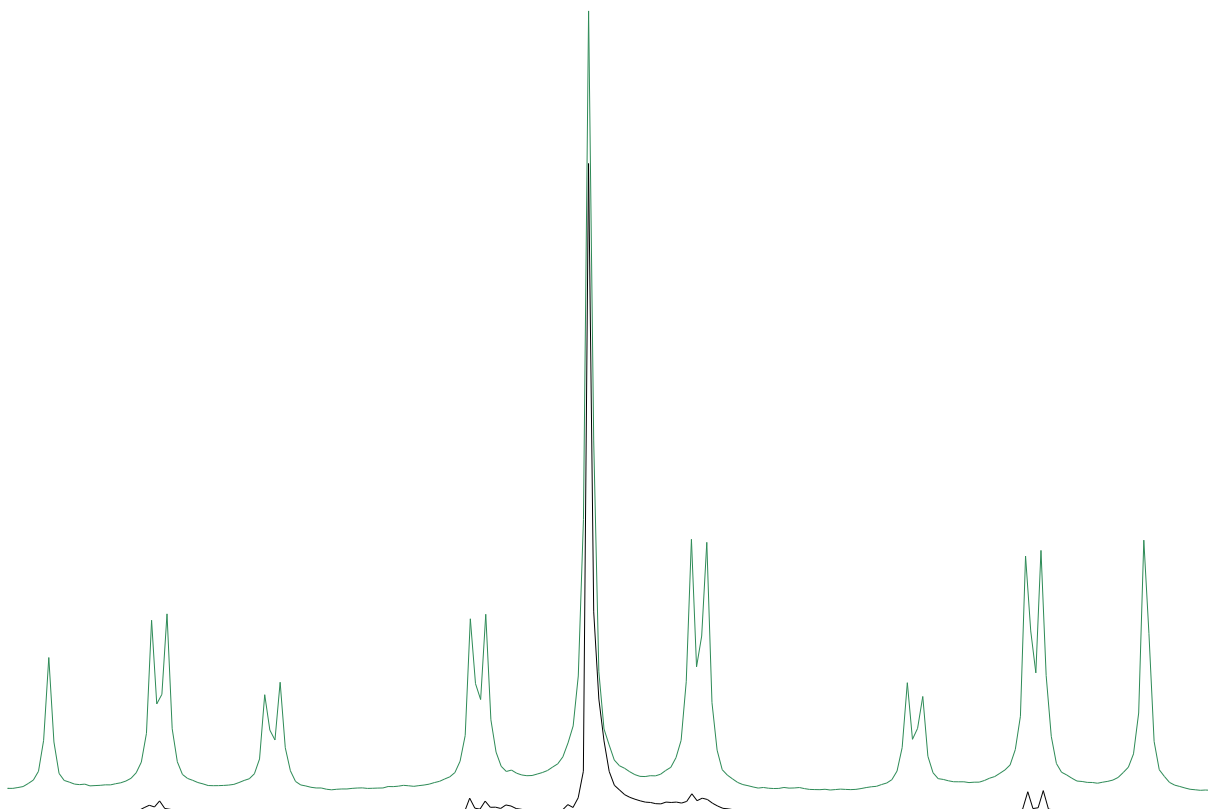


Figure 18 - Superposition of Degraded Purified and Ultra-Purified CYANEX® 301 0.1M in Toluene - ^1H Decoupled ^{31}P NMR - Insert H_3PO_4 0.1M in D_2O

2. Explanation of the multiplicity peaks

The presence of asymmetric carbons in the two alkyl chains creates a different environment for the phosphorus as demonstrated by the two peaks in the pristine compound of CYANEX® 301 (and 272) before contact with nitric acid. When bridging two phosphorus through a disulfide bond, the phosphorus atoms become asymmetric themselves and can be coupled if they are not equivalent.

The asymmetry of the phosphorus atoms in the disulfide was studied. Indeed, the Cahn Ingold and Prelog theory indicates that in the case of a carbon atom, this atom is asymmetric, even if it is linked with two identical alkyl chains, with the condition that these alkyl chains contain an asymmetric carbon atom, and that the stereodescriptors of these atoms are different between the two chains. The spatial representation of the disulfide is presented in Figure 19.

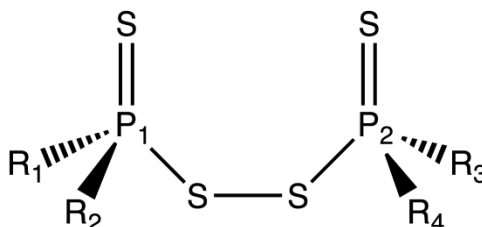


Figure 19 - Spatial representation of the disulfide

It can be reasonably assumed that this theory can be applied to phosphorus atoms. It was hypothesized that the sulfur linked with a double bond to the phosphorous is the atom determining the direction for the allocation of a stereodescriptor (Figure 20). The priority of the other substituents is determined using the rules applied for carbon, i.e., in the case of two identical alkyl chains with different stereodescriptors for the asymmetric carbons on the chains, R has the priority on over S. In the disulfide, each phosphorus atom can be assigned three different stereodescriptors. Indeed, if the two alkyl chains have the same stereodescriptor on their asymmetric carbon atoms, it will not be possible to give the priority to one chain on the other, and the phosphorus is in this case non-asymmetric (written NAs in the rest of the text).

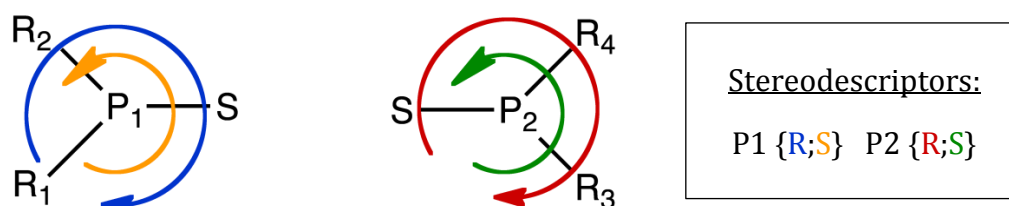


Figure 20 - Determination of the stereodescriptors of the phosphorus

With these rules, stereodescriptors have been allocated to all phosphorus atoms, and all possible combinations are presented in Table 1.

Phosphorus 1	Phosphorus 2	P Asymmetry
[R;R]	[R;R]	[NAs;NAs]
[R;R]	[S;S]	[NAs;NAs]
[R;R]	[R;S]	[NAs;S]
[R;R]	[S;R]	[NAs;R]

Allocation	
Asymmetry P	[P ₁ ;P ₂]
Phosphorus 1	[R ₁ ;R ₂]
Phosphorus 2	[R ₃ ;R ₄]

[S;S]	[R;R]	[NAs;NAs]
[S;S]	[S;S]	[NAs;NAs]
[S;S]	[R;S]	[NAs;S]
[S;S]	[S;R]	[NAs;R]

[R;S]	[R;R]	[R;NAs]
[R;S]	[S;S]	[R;NAs]
[R;S]	[R;S]	[R;S]
[R;S]	[S;R]	[R;R]

[S;R]	[R;R]	[S;NAs]
[S;R]	[S;S]	[S;NAs]
[S;R]	[R;S]	[S;R]
[S;R]	[S;R]	[S;S]

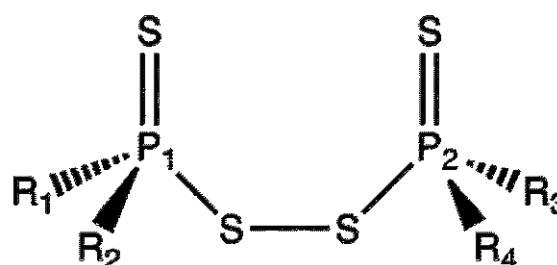
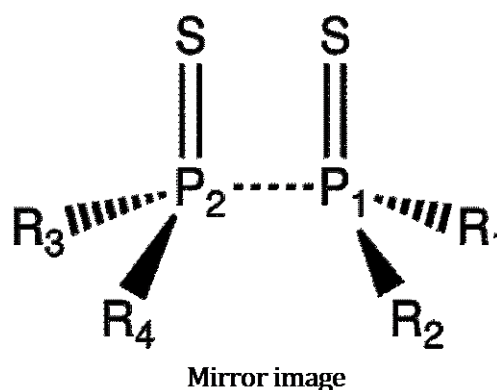
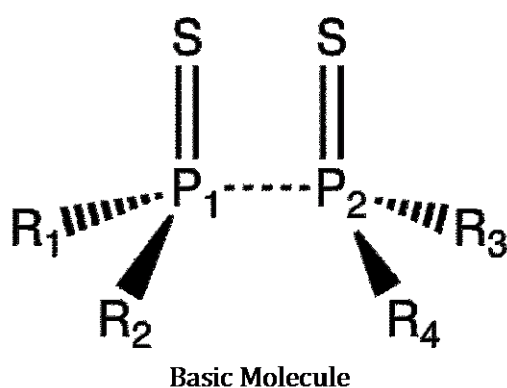


Table 1 - List of possible combinations of isomers

This study has led to sixteen different combinations for the molecule. But, a closer look at the asymmetry of the phosphorus atom affords some combinations including couples of enantiomers, diastereoisomers, and isomers...

The determination of the couples is presented in Table 2.

Mirror					
Phosphorus 1	Phosphorus 2	P Asymetry	Phosphorus 1	Phosphorus 2	P Asymetry
[R;R]	[R;R]	[NAs;NAs]	[S;S]	[S;S]	[NAs;NAs]
[R;R]	[S;S]	[NAs;NAs]	[S;S]	[R;R]	[NAs;NAs]
[R;R]	[R;S]	[NAs;S]	[S;S]	[S;R]	[NAs;S]
[R;R]	[S;R]	[NAs;R]	[S;S]	[R;S]	[NAs;R]
[S;S]	[R;R]	[NAs;NAs]	[R;R]	[S;S]	[NAs;NAs]
[S;S]	[S;S]	[NAs;NAs]	[R;R]	[R;R]	[NAs;NAs]
[S;S]	[R;S]	[NAs;S]	[R;R]	[S;R]	[NAs;S]
[S;S]	[S;R]	[NAs;R]	[R;R]	[R;S]	[NAs;R]
[R;S]	[R;R]	[R;NAs]	[S;R]	[S;S]	[R;NAs]
[R;S]	[S;S]	[R;NAs]	[S;R]	[R;R]	[R;NAs]
[R;S]	[R;S]	[R;S]	[S;R]	[S;R]	[R;S]
[R;S]	[S;R]	[R;R]	[S;R]	[R;S]	[R;R]
[S;R]	[R;R]	[S;NAs]	[R;S]	[S;S]	[S;NAs]
[S;R]	[S;S]	[S;NAs]	[R;S]	[R;R]	[S;NAs]
[S;R]	[R;S]	[S;R]	[R;S]	[S;R]	[S;R]
[S;R]	[S;R]	[S;S]	[R;S]	[R;S]	[S;S]



[Table 2 - Determination of the couples of enantiomers and diastereoisomers](#)

The different combinations of isomers have been organized according to the stereodescriptors of the phosphorus atoms. The initial mixture of CYANEX® 301 was assumed to be a perfect racemic mixture, with the isomers {[R;R];[S;S];[R;S];[S;R]} in equal proportions. This hypothesis has led to the allocation of probabilities of formation for each group, which are presented in Table 3.

Case	Comments	Formation probability
[NAs;NAs]	Made of two enantiomers {[S;S];[S;S]} and {[R;R];[R;R]} and their diastereoisomers, which are in fact one molecule {[R;R];[S;S]} (a rotation gives {[S;S];[R;R]}) . Possibility to distinguished the diastereoisomers in NMR in some cases.	4
[NAs;R] and [R;NAs]	Made of only two enantiomers {[R;S];[RR]} and {[R;S];[S;S]}, these two possibilities are equivalent (considering one enantiomer, a rotation can change [NAs;R] in [R;NAs], and reversly).	4
[NAs;S] and [S;NAs]	Made of only two enantiomers {[S;R];[RR]} and {[S;R];[S;S]}, these two possibilities are equivalent (considering one enantiomer, a rotation can change [NAs;S] in [S;NAs], and reversly).	4
[R;R] and [S;S]	Each of these two possibilities is made with only one molecule (it is impossible to distinguish the two phosphorus when they have the same stereo-descriptor). [R;R] and [S;S] are "double" diastereoisomers : considering alkyl chains, and phosphorus.	1 Each
[R;S] and [S;R]	These two possibilities are in fact only one molecule. The couples {[R;S];[R;S]} and {[S;R];[S;R]} are equivalent.	2

[Table 3 - Group of asymmetric phosphorus and probabilities of formation](#)

Thus, assuming that there is coupling between two phosphorus atoms in the molecule when their stereodescriptors are different and the probability of formation of each couple, the different peaks were assigned as presented in Table 4. Integration of the peaks corroborated the assignment.

Case	Number of peaks	Total intensity	Attribution (ppm)
[NAs;NAs]	1 (Possibly two)	4	79,424
[X;NAs] & [NAs;X]	4 (Doublet of doublet)	4	NAs ↔ X {79,582;79,607} X ↔ NAs {80,074;80,099}
[Y;NAs] & [NAs;Y]	4 (Doublet of doublet)	4	NAs ↔ Y {79,243;79,265} Y ↔ NAs {78,727;78,752}
[X;X]	1	1	80,257
[Y;Y]	4	1	78,571
[X;Y] & [Y;X]	4 (Doublet of doublet)	2	X ↔ Y {79,900;79,924} Y ↔ X {78,910;78,935}

X & Y = R or S

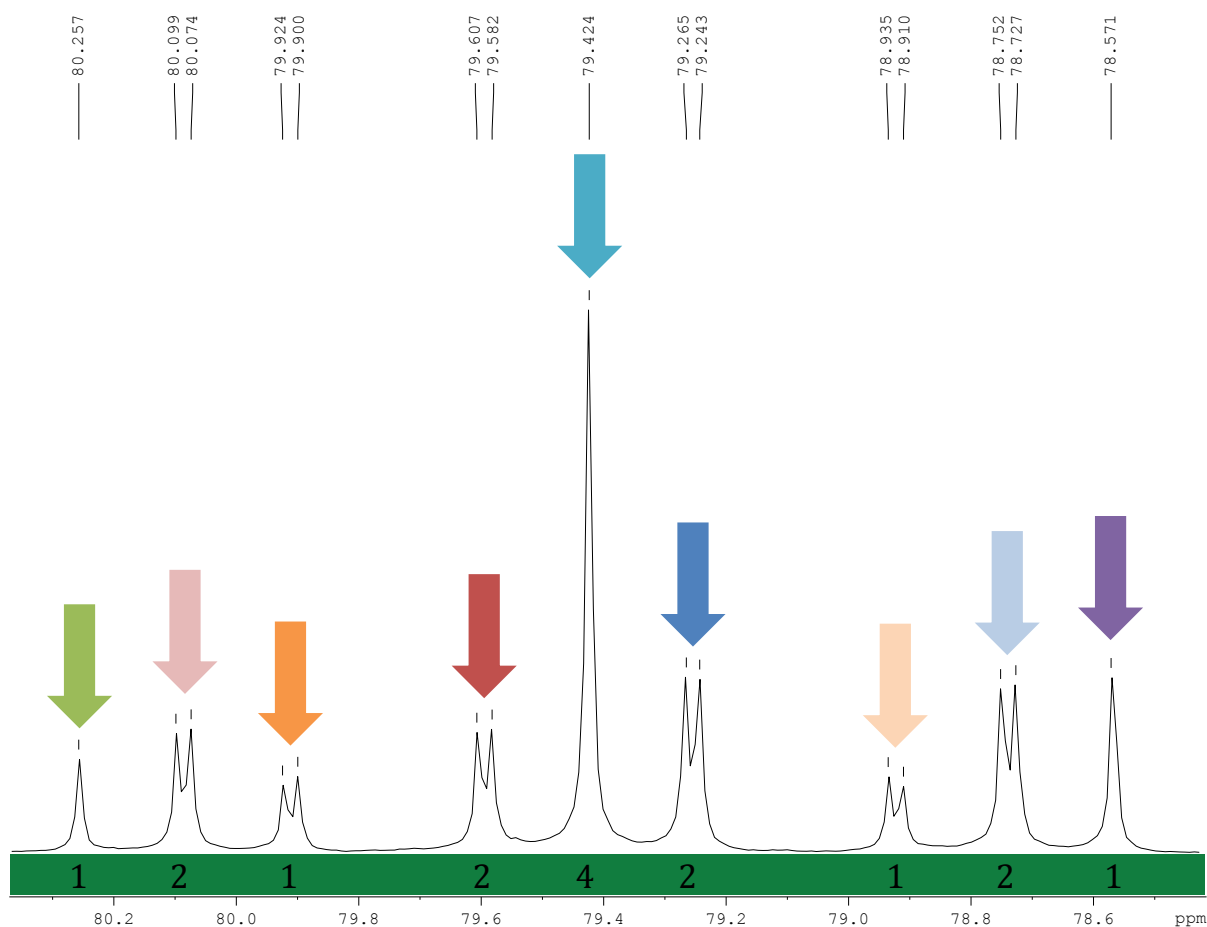


Table 4 - Allocation of the asymmetric groups to the peaks

It is interesting to point out that this assignment also explains many details we observe on the spectrum.

First, a closer look at the spectrum of the degradation of the ultra-purified CYANEX® 301 (Figure 17) shows small doublets in addition to the main peak. These correspond to the coupling of NAs phosphorus with either R or S phosphorus. This supports the explanation above, as there are likely traces of [R;S] and [S;R] molecules of CYANEX® 301 remaining after ultra-purification. Thus, with these isomers only at trace levels, the most probable disulfide bridged products are with a non-asymmetric phosphorus, and therefore these peaks correspond to the couples [NAs;R] or [NAs;S].

The other point is that, depending on the solvent, the central peak can split (Figure 21). This can be explained by the fact that the couple [NAs;NAs] is made of four different combinations. Two of these combinations are enantiomers, the two other are also a couple of enantiomers. And these two enantiomeric couples are diastereoisomers of each other, which can probably explain the possible presence of two peaks for the couple [NAs;NAs] (two peaks also appear for the diastereoisomers for CYANEX® 301, and CYANEX® 272).

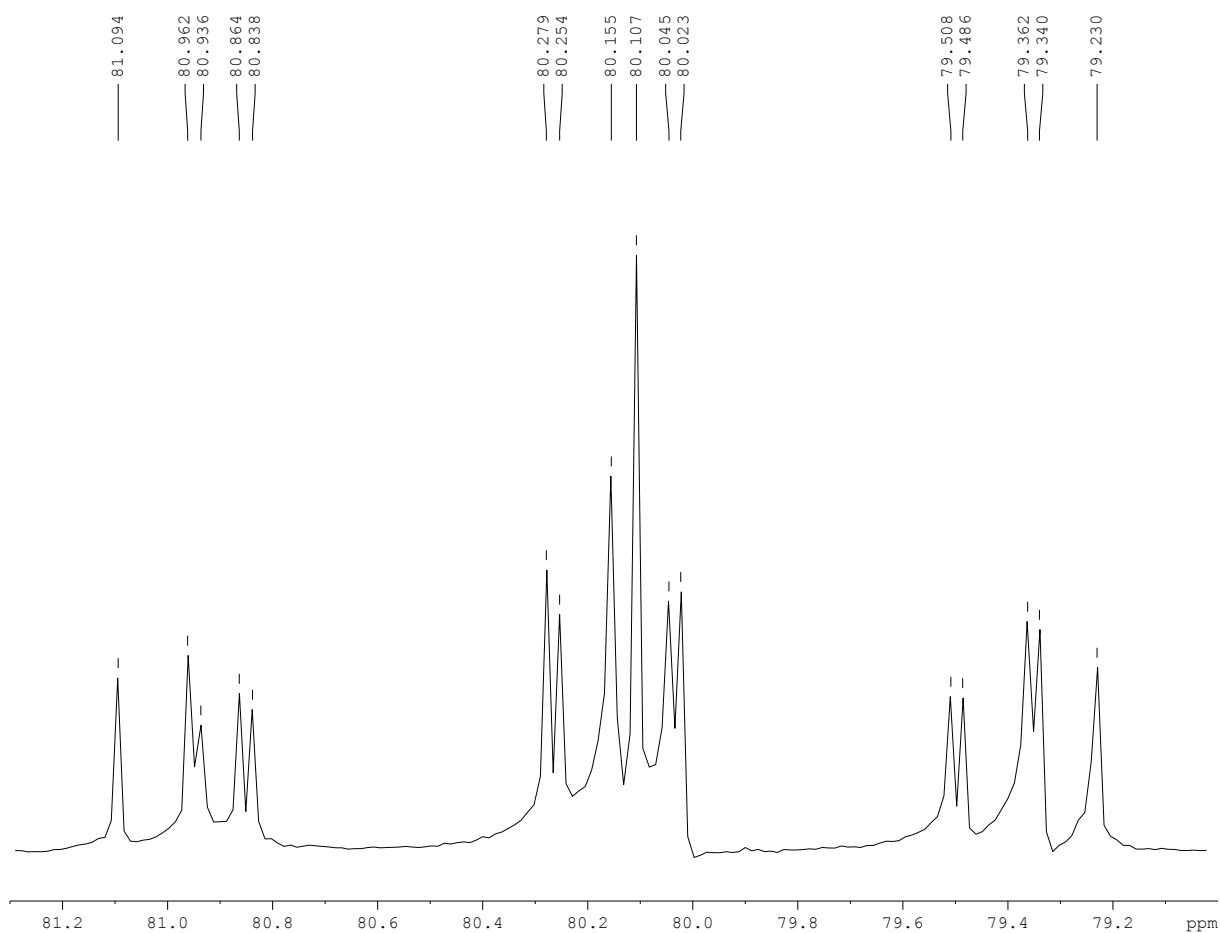


Figure 21 – Degradation product of CYANEX®301 0.1M in CDCl₃ – ¹H Decoupled ³¹P NMR – Insert H₃PO₄ 0.1M in D₂O

3. Validation of the coupling of phosphorus nuclei

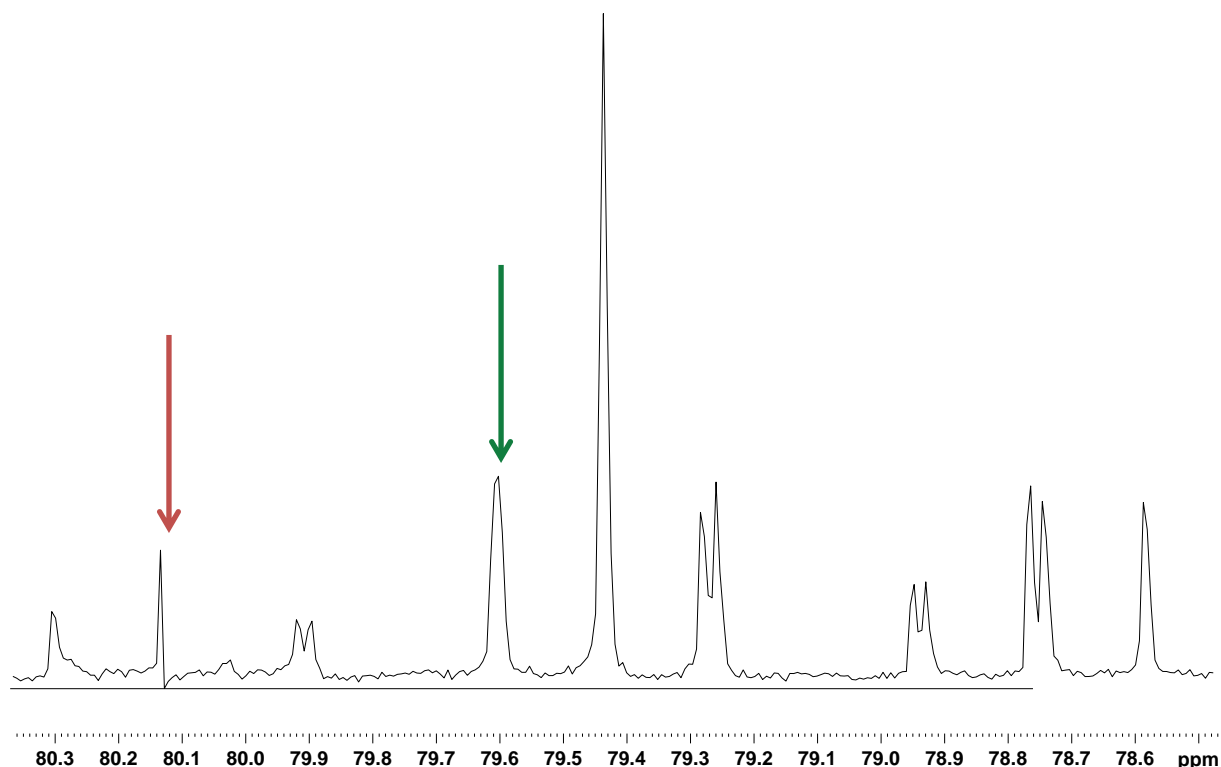
To ensure the multiplicity of some peaks (doublets) was a consequence of a coupling with other phosphorus present in the S-bridged molecule and also to validate the identification of the couples of phosphorus nuclei coupled to each other, ^{31}P homodecoupled NMR was used: this method is commonly used in ^1H NMR, but relatively unusual in ^{31}P NMR.

The new NMR of the Chemical Science Division, which is equipped of three channels, was used. These channels were used as follow:

- Channel 1: Excitation of the phosphorus atoms
- Channel 2: Irradiation of the phosphorus at a given frequency (Homodecoupling)
- Channel 3: Irradiation of the protons (^1H decoupling)

The result of this homodecoupling is that the peak corresponding to the irradiated phosphorus will disappear, and, if the multiplicity is really a result of a coupling with another phosphorus nucleus, there must be one of the other doublets which will become a singlet, affording the identification of the couples of coupled phosphorus atoms.

The results of these experiments are presented in the figures below. The red arrow indicates the frequency of irradiation (peak annihilated due to the irradiation of the corresponding phosphorus), and the green one points out the peak becoming a singlet.



[Figure 22 – \$\{^1\text{H}, ^{31}\text{P}\}\$ Homodecoupled \$^{31}\text{P}\$ NMR – Validation of the coupling \$\[\text{NAs};\text{X}\]\$ & \$\[\text{X};\text{NAs}\]\$](#)

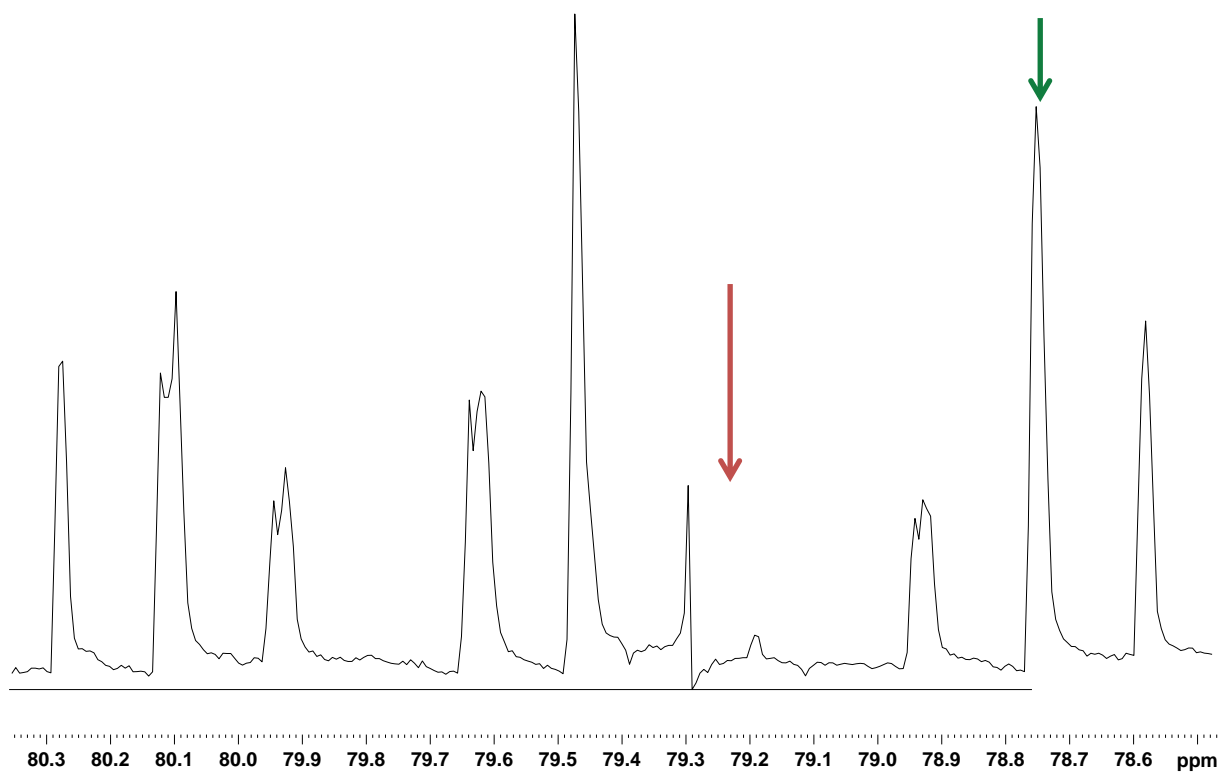


Figure 23 - $\{^1\text{H}, {}^{31}\text{P}\}$ Homodecoupled ${}^{31}\text{P}$ NMR – Validation of the coupling [NAs;Y] & [Y;NAs]

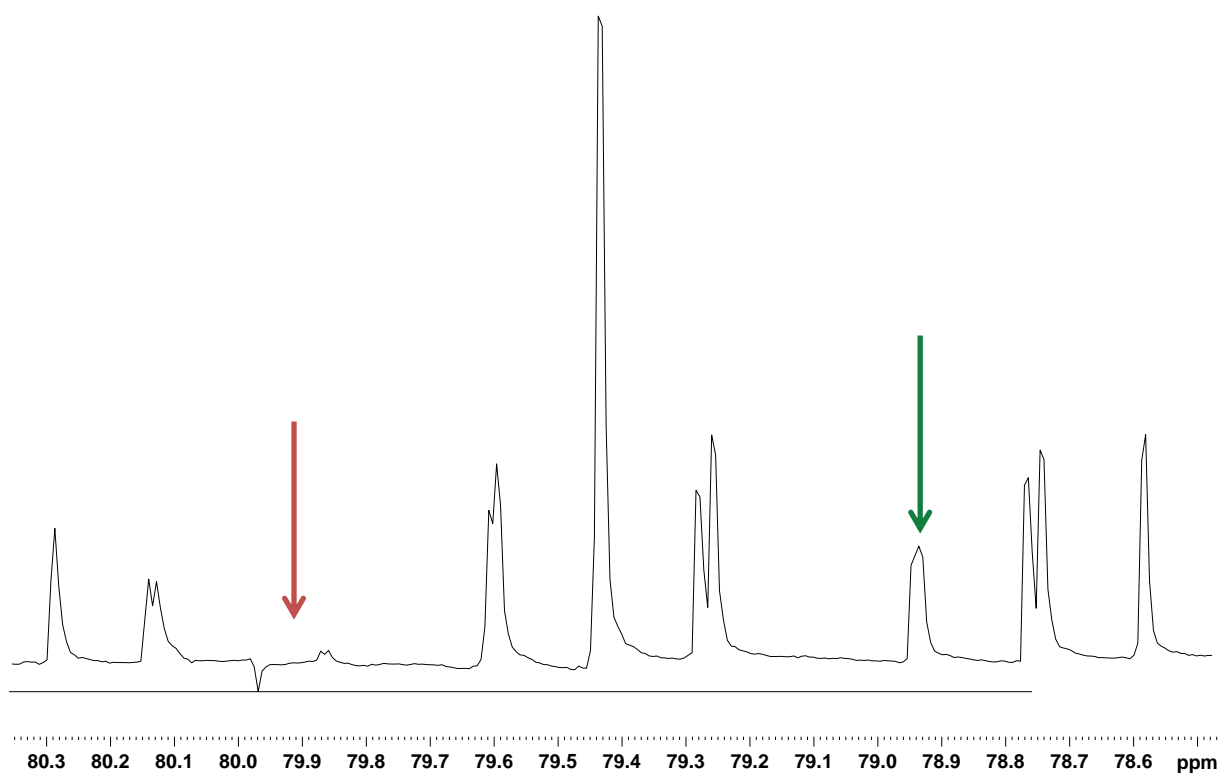
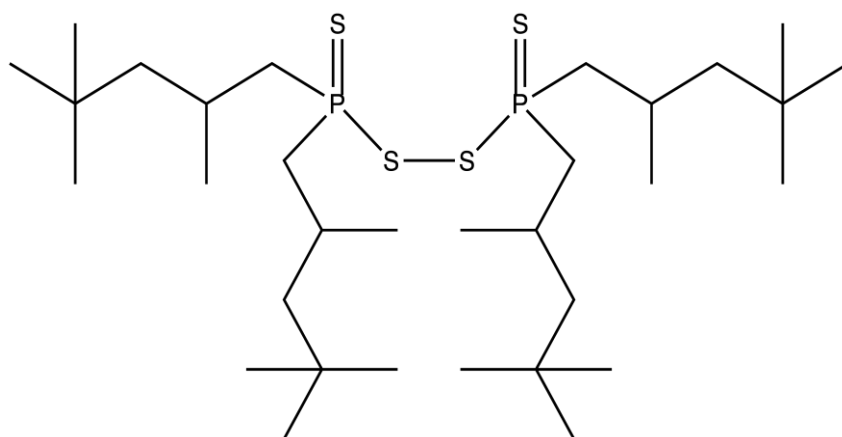


Figure 24 - $\{^1\text{H}, {}^{31}\text{P}\}$ Homodecoupled ${}^{31}\text{P}$ NMR – Validation of the coupling [Y;X] & [X;Y]

This series of experiments validates the identification of the coupled. The spectra show a shift in frequency of most peaks towards the frequency of irradiation. This phenomenon is called the *Bloch Steric Effect*.

4. Elemental analysis of the degradation product

The degradation product was isolated, and was sent for elemental analysis. The result and comparison with the theory of this analysis are presented in Table 5.



Number of carbon	32
Number of phosphorus	2
Number of hydrogen	68
Number of sulfur	4
Number of oxygen	0
Number of nitrogen	0

Molecular weight (g/mol) 643,0972

	Calculated Mass %	Analyzed	Delta
Carbon	59,77%	58,65%	1,12%
Phosphorus	9,63%	8,61%	1,02%
Hydrogene	10,66%	9,92%	0,74%
Sulfur	19,94%	18,57%	1,37%
Oxygene	0,00%	NA	IR
Nitrogene	0,00%	< 0.5%	IR
Total	100,00%	95,75%	4,25%

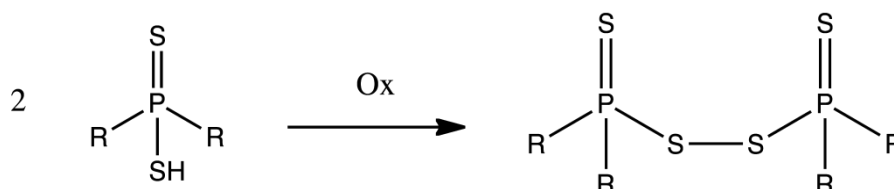
Table 5 - Results of the elemental analysis and comparison with the theoretical mass percentages

These results are consistent with the hypothesis of the formation of a disulfide bridge. The missing 4.25% on the total mass can probably be assigned to the presence of oxygen as the NMR spectrum of the product sent to Galbraith showed a small amount of CYANEX® 272.

III. Elements on the first step pathway of the degradation

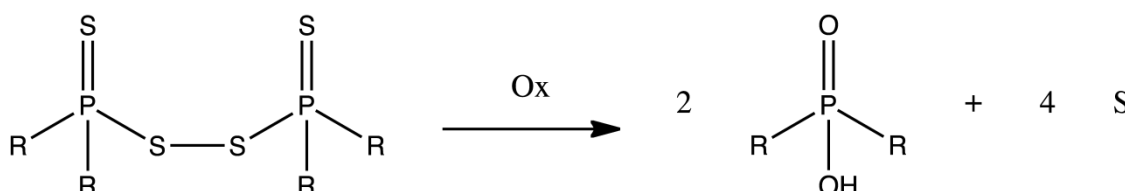
1. General mechanism of the degradation

It is reasonable to assume that the first step of the degradation with nitric acid is an oxidation of two molecules of CYANEX® 301, leading to the formation of a disulfide bridge:



[Figure 25 - First step of the degradation of CYANEX® 301](#)

The second step consists in another oxidation of the disulfide, which leads to two molecules of CYANEX® 272 and elemental sulfur. This second step has been described using hydrogen peroxide to oxidize the disulfide [13]:






[Figure 26 - Second step of the degradation of CYANEX® 301](#)

It is important to point out that this mechanism can be observed for concentrations in nitric acid lower than 4 mol/l.

2. Role of the acid and the oxidizer

The role of the acid and of the oxidizer was studied. Experiment with only an acid (HCl), with an acid that has oxidizing properties (HNO₃), with the same acid with another oxidizer (HNO₃ + NaNO₂), and just the oxidizer (NaNO₃ + NaNO₂) were run. The results of degradation are presented in Table 6.

CYANEX 301 contacted with	Analysis after	
	30 minutes	3 hours
HCl 1M		ND
HNO ₃ 1M	PD	CD
HNO ₃ 1M + NaNO ₂ 10mM	CD	
NaNO ₃ 1M + NaNO ₂ 10mM		ND

ND : No Degradation

PD : Partial Degradation

CD : Complete Degradation

[Table 6 - Influence of the acid and oxidizer on the degradation](#)

These results clearly show that the mechanism involves both an acid and an oxidizer. A complete degradation of the compound with nitric acid 1M is obtained after 3 hours. The addition of a stronger oxidizer gives a complete degradation only after 30 minutes.

3. Influence of the atmosphere on the degradation

Depending on the atmosphere, more precisely on the presence or not of oxygen, the degradation could be complete or null. The results of the tests under different atmospheres are presented in Table 7.

Atmosphere	Analysis after 3 hours
Open to air	CD
Sealed under air	CD
Sealed under Ar	ND

ND : No Degradation
PD : Partial Degradation
CD : Complete Degradation

Table 7 - Influence of the atmosphere on the degradation

The presence of oxygen appears to have a role in the degradation of CYANEX® 301. Considering that the formation of NO₂ has been observed when a large amount of CYANEX® 301 is degraded, it is possible that nitrogen monoxide could be a by-product of the degradation step leading to the disulfide. Thus, the oxygen present in the atmosphere will react with the nitrogen monoxide to form nitrogen dioxide. This transformation of a by-product could be responsible of the displacement of the equilibrium to the formation of more disulfide. Degradation under a stream of argon or with argon atmosphere renewing would remove the nitrogen monoxide from the tank, while maintaining an anoxic environment. If the degradation is complete, this would be another element supporting this hypothesis.

4. Suggested mechanism

Considering these two studies, and the semi-electronic redox reactions, the following mechanism is proposed for the first step of the degradation:

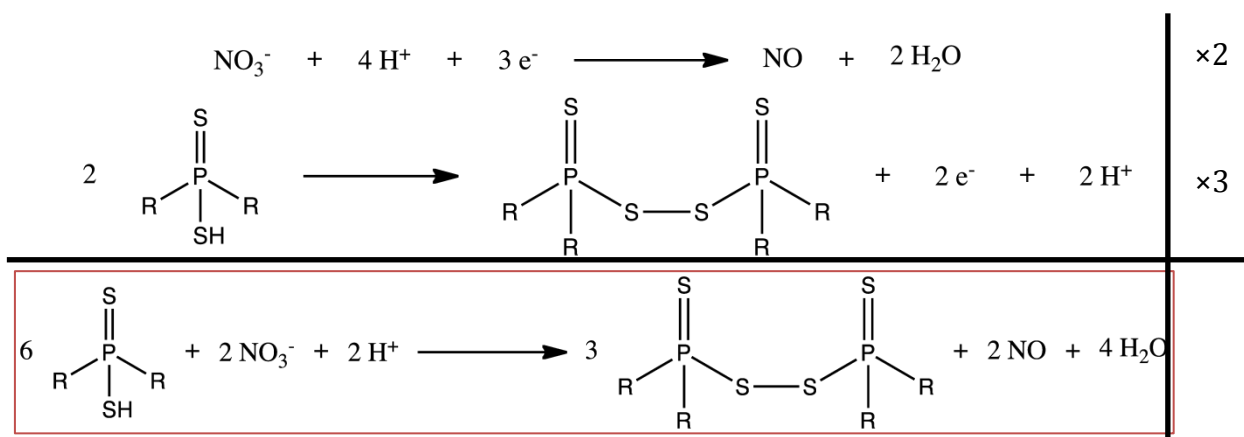
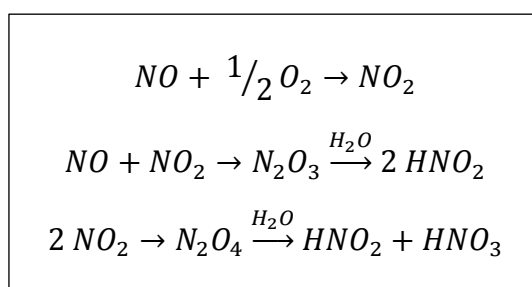


Figure 27 - Proposal of pathway for the first step of the degradation

It is important to remember that this is only a suggestion. It is mandatory to perform other experiments to validate this hypothesis, but it is also important to see that this equation can explain why it is required to have an acid (appears in the equation as a reagent), an oxidizer (a reagent too), where nitrogen monoxide comes from, and why its removal by reaction with oxygen can help forming more disulfide (the removal of a by-product will yield to the displacement of the equilibrium to the formation of more products).

The role of the oxygen, and its probable reaction with nitrogen monoxide could be double: it seems that the formation of nitrogen dioxide, product of this reaction, could yield to refuel the solution with oxidative species such as nitric acid (HNO_3) and nitrous acid (HNO_2), following the reactions presented in Figure 28:



[Figure 28 - Regeneration of oxidizer by the reaction of \$\text{NO}_2\$](#)

But, the lack of equilibrium constant values and the lack of demonstration that these reactions do occur in our experiments make these hypotheses arguable. They are more pathways that could be interesting to investigate in order to find out how oxygen can impact the degradation of CYANEX® 301.

Conclusion

The aim of this work was to study the degradation of dithiophosphinic acids contacted with nitric acid. To conduct this project, we have used the bis(2,4,4-trimethylpentyl)dithiophosphinic acid.

The first objective was to figure out what compound was obtained after contact with nitric acid. It was identified without ambiguity that the product is a dimer of bis(2,4,4-trimethylpentyl)dithiophosphinic acid, with two molecules of the original compound being linked by a disulfide bridge.

The identification of this product afforded an explanation in details of the complex ^{31}P NMR spectrum we obtained for the degradation product. The multiplicity of the peaks was found to have for origin the existence of different stereoisomeric states of the phosphorous nuclei in the disulfide.

Solving these points has led to start a study on the mechanism of the formation of the disulfide. Even if it is still too early to propose a definitive mechanism, one can be reasonably suggested based on the experimental evidences collected so far.

On a more personal point of view, I would say that this internship has been for me the occasion to go into the use of the NMR technique in depth, even if the last presented analyses using homodecoupling remind me that I still have lots of things to learn about this instrument. I have also been able to discover separative chemistry, and how research is conducted to discover new molecules to solve the challenges posed by the extraction and separation of minor actinides.

It has also been an opportunity to discover the United States of America, more precisely Tennessee, and the system of National Laboratories.

And last but not least, I have been able to meet all the people of the Chemical Separation Group, whom I would like to thank again for their warm welcome, and all the good moments of these last six months.

Note: This is not the definitive report. We have already run other experiments, not presented here, and will probably run many others during the next few weeks. The corresponding results will be added to this report.

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Appendix

I. Purification process of CYANEX® 301

The purification process of CYANEX® 301 is a four day long procedure, respecting the following step:

- Day 1: 52 g of commercial CYANEX® 301 are added to 200 ml of benzene in a 500 ml round bottom flask. The solution is stirred and heated to 70 °C. Then, 14 g of ammonium carbonate are added in portions to the solution. After all the carbonate is added, the solution is stirred for 4 hours at 70 °C. The solution is then filtered hot on a fritted funnel, and was let to cool down to room temperature before being put in a refrigerator overnight.
- Day 2: The entire solution is found to be a solid mass of crystals in the morning. The mass is filtered on a fritted funnel, and the filter cake dried at room temperature using the vacuum provided by a rotary evaporator. 200 ml are added to the dry solid, which is re-dissolved using the agitation of the rotary evaporator, and the heating of the bath. Once the entire solid is dissolved, the solution is filtered hot on a fritted funnel, was let cool to room temperature, and then placed in a refrigerator overnight.
- Day 3: The entire solution is found to be a solid mass of crystals in the morning. The mass is filtered on a fritted funnel, and the filter cake dried at room temperature using the vacuum provided by a rotary evaporator. 200 ml are added to the dry solid, which is re-dissolved using the agitation of the rotary evaporator, and the heating of the bath. Once the entire solid is dissolved, the solution is filtered hot on a fritted funnel, was let cool to room temperature, and then placed in a refrigerator overnight.
- Day 4: The entire solution is found to be a solid mass of crystals in the morning. The mass is filtered on a fritted funnel, and the filter cake dried at room temperature using the vacuum provided by a rotary evaporator. The obtained mass was about 30 g. This mass is put in a 1 l separatory funnel, and dissolved in 45 ml of ethanol and 300 ml of petroleum ether while swirling the funnel. This organic solution is contacted twice with 250 ml of 4M HCl, and washed three times with nanopure water (the pH of the water wash was about 5). The organic phase is then transfer in an erlenmeyer, and sodium sulfate has been added to the flask until the organic phase was dry. The solution is then filtered into a round bottom flask, and the solvent removed using a rotary-evaporator. The product was a green oil, found to be pure Bis(2,4,4-trimethylpentyl)dithiophosphinic acid by NMR analysis (Figure 10).

II. Elemental Analysis Report

Report Number: 35123



Report Date: 2011-08-22

Laboratory Report

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Sample: JPCC8882		Received: 2011-08-10			
Lab ID: 2011-O-9383					
Analysis	Method	Result	Basis	Amount	Date (Time)
C : Carbon	GLI Procedure ME-3	58.65 %	As Received	2.268 mg	2011-08-16
	GLI Procedure ME-3	9.92 %	As Received	2.268 mg	2011-08-16
H : Hydrogen	GLI Procedure ME-3	< 0.5 %	As Received	2.268 mg	2011-08-16
	GLI Procedure ME-3	< 0.5 %	As Received	2.268 mg	2011-08-16
N : Nitrogen	GLI Procedure ME-3	< 0.5 %	As Received	2.268 mg	2011-08-16
	GLI Procedure ME-3	< 0.5 %	As Received	2.268 mg	2011-08-16
P : Phosphorus	GLI Procedure ME-70	8.61 %	As Received	131.69 mg	2011-08-12
	GLI Procedure ME-70	8.61 %	As Received	131.69 mg	2011-08-12
S : Sulfur	GLI Procedure E16-2	18.57 %	As Received	13.02 mg	2011-08-12
	GLI Procedure E16-2	18.57 %	As Received	13.02 mg	2011-08-12

For all samples on this report:

1. We regret that we cannot determine oxygen in the presence of relatively high concentrations of phosphorus.

Signatures:

Published By: pat.b.delozier

2011-08-22T18:55:00.91-04:00

- Physical signatures are on file.
- "Published By" signature indicates authorized release of data.

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III. Instruments used

NMR experiments were run either on a Bruker Avance 400 or on a Bruker Avance III 400.

The latter instrument was used for the ^{31}P homonuclear decoupling.



[Figure 29 - Bruker Avance 400](#)



[Figure 30 - Bruker Avance III 400](#)